

Stability of supercooled binary liquid mixtures

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The supercooled Kob-Andersen binary Lennard-Jones (KABLJ) mixture crystallizes partially in lengthy computer simulations by forming pure FCC crystals of the majority component. The general thermodynamic and kinetic stability of supercooled binary mixtures is discussed, emphasizing the importance of negative mixing enthalpy whenever present. Based on this a modification of the KABLJ mixture is proposed that is less prone to crystallization and faster to simulate; this is obtained by removing the like-particle attractions by switching to Weeks-Chandler-Andersen type potentials while maintaining the unlike-particle attraction.

I. INTRODUCTION

As computers get faster, simulations of the highly viscous liquid phase preceding glass formation become increasingly realistic. In this context it is nice to have a standard model system, something like the Ising model for critical phenomena. For several years binary Lennard-Jones (BLJ) mixtures have served this purpose – in particular the Wahnström and Kob-Andersen systems [1, 2], because they are easy to simulate and were never found to crystallize. The Kob-Andersen BLJ consists of two types of Lennard-Jones particles, 80% large (A) particles and 20% small (B) particles. The BLJ potentials are modifications of the potentials devised by Weber and Stillinger [3], who constructed the pair potentials for the binary mixture based of physical-chemical data for the $\text{Ni}_{80}\text{P}_{20}$ alloy. The Kob-Andersen potentials describe a strongly non-ideal mixture due to an AB attraction that is three times stronger than the BB attraction. This ensures a large negative mixing enthalpy (and energy), which suppresses crystallization into pure A crystals as detailed below.

Recently, both the Wahnström (Wa) and the Kob-Andersen (KA) systems were shown to crystallize in lengthy computer runs [4]. This motivated the present paper that has three purposes. First, we briefly review the general theory of thermodynamic and kinetic stability of supercooled binary mixtures (Sec. II). Secondly, we detail the crystallization of the Kob-Andersen systems (Sec. III), while the crystallization of the Wahnström liquid will be described elsewhere [5]. Finally, we suggest a modification of the KA binary system that is more stable and faster to simulate; in fact, we have not been able to crystallize the new system even in month long simulations. The idea is to keep the KA system's large negative mixing enthalpy, but remove the AA and BB attractions by adopting Weeks-Chandler-Andersen (WCA) type potentials between like particles (Sec. IV). Section V gives a brief discussion.

II. GENERAL TREATMENT

Consider a binary mixture of N_A solvent (A) particles and N_B solute (B) particles, with total number of particles $N = N_A + N_B$. The thermodynamic stability of this system against crystallization is expressed by the melting temperature of a pure A crystal, $T_{\text{fus,A}}$, as a function of the concentration of A particles. The latter quantity is conveniently expressed in terms of the fraction $x_B = N_B/N$ of B particles ($x_A + x_B = 1$). We consider the usual case of externally controlled temperature T and pressure p . At the melting temperature of the pure A crystalline phase in the AB mixture, the chemical potential of the A particles in the crystal equals the chemical potential of the A particles of the liquid mixture. The chemical potential is the Gibbs free energy per particle. The change in Gibbs free energy per A particle at melting, $\Delta G_{\text{trans,A}}$ can be divided into two terms, $\Delta G_{\text{fus,A}}$ and $\Delta G_{\text{mix,A}}$, where $\Delta G_{\text{fus,A}}$ is the change in Gibbs free energy per A particle upon melting an A crystal into pure A liquid, and $\Delta G_{\text{mix,A}}$ is the change in Gibbs free energy per A particle going from pure to mixed liquid. The melting temperature $T_{\text{fus,A}}$ is determined by

$$\Delta G_{\text{trans,A}} = \Delta G_{\text{fus,A}}(T_{\text{fus,A}}) + \Delta G_{\text{mix,A}}(T_{\text{fus,A}}) = 0. \quad (1)$$

The case of pure A ($x_B = 0$) will be denoted by an asterisk, thus $T_{\text{fus,A}}^*$ is the melting point of the pure A crystal

into pure A liquid. In this case $\Delta G_{\text{trans,A}} = \Delta G_{\text{fus,A}}^*$ and since $G = H - TS$, one has $\Delta H_{\text{fus,A}}^* - T_{\text{fus,A}}^* \Delta S_{\text{fus,A}}^* = 0$ where here and henceforth all thermodynamic quantities are per A atom. In the general case where $x_B \neq 0$ one has $\Delta H_{\text{fus,A}} - T_{\text{fus,A}} \Delta S_{\text{fus,A}} = -\Delta G_{\text{mix,A}}$. When deriving the standard expression for the freezing point depression one makes the approximation that crystal and liquid have the same specific heats, i.e that $\Delta H_{\text{fus,A}}$ and $\Delta S_{\text{fus,A}}$ are temperature independent. Selfconsistently with this we assume that $\Delta H_{\text{mix,A}}$ and $\Delta S_{\text{mix,A}}$ temperature independent. Writing $T_{\text{fus,A}} = T_{\text{fus,A}}^* - \Delta T_{\text{fus,A}}$, where $\Delta T_{\text{fus,A}}$ is the melting point depression due to the presence of B particles and via $\Delta H_{\text{fus,A}} = T_{\text{fus,A}}^* \Delta S_{\text{fus,A}}$, this implies that $\Delta T_{\text{fus,A}} \Delta S_{\text{fus,A}} = -\Delta G_{\text{mix,A}}$, and

$$\frac{\Delta T_{\text{fus,A}}}{T_{\text{fus,A}}^*} = -\frac{\Delta G_{\text{mix,A}}}{\Delta H_{\text{fus,A}}}. \quad (2)$$

In the standard textbook treatment one assumes that $\Delta H_{\text{mix,A}} = 0$ and that the mixing entropy is ideal, i.e., that the mixing entropy divided by $N = N_A + N_B$ is given by $\Delta S_{\text{mix}} = -k_B[x_A \ln(x_A) + x_B \ln(x_B)]$. This expression separates into a contribution from the A particles and one from the B particles. Per A particle we thus have $\Delta S_{\text{mix,A}} = -k_B \ln(x_A) = -k_B \ln(1 - x_B)$. In the limit $x_B \rightarrow 0$ Eq. (2) under these assumptions reduces to the well-known expression

$$\frac{\Delta T_{\text{fus,A}}}{T_{\text{fus,A}}^*} \cong \frac{k_B T_{\text{fus,A}}}{\Delta H_{\text{fus,A}}^*} x_B. \quad (3)$$

More generally, $\Delta H_{\text{mix,A}} = 0$ does not apply – in fact for the Kob-Andersen liquid the mixing enthalpy is large (and negative) and this term cannot be ignored. The mixing entropy, on the other hand, is still realistically given by $\Delta S_{\text{ideal mix,A}}$. For this more general case Eq. (2) becomes

$$\frac{\Delta T_{\text{fus,A}}}{T_{\text{fus,A}}^*} = -\frac{\Delta H_{\text{mix,A}} + k_B T_{\text{fus,A}} \ln(x_A)}{\Delta H_{\text{fus,A}}}. \quad (4)$$

A negative mixing enthalpy clearly implies a further melting point depression beyond that of the traditional treatments. If there is a large negative mixing enthalpy, this effect is important.

The stability of a supercooled liquid mixture depends not only on its absolute (thermodynamic) stability against crystallization, but is also affected by kinetic effects. Thus the less supercooled the liquid is, the larger is the critical nucleus and the more stable is the liquid. This means that it takes longer time before a critical nucleus is generated by a thermal fluctuation, i.e., the supercooled liquid is more stable. At a given temperature the supercooled liquid is more stable the more negative $\Delta G_{\text{mix,A}}$ becomes. To see this divide the creation of a crystal nucleus of pure A particles in the mixture

$$N_A(\text{mix}) \rightarrow N_A(\text{crystal}, x_A = 1) \quad (5)$$

into two steps:

$$\begin{aligned} N_A(\text{mix}) &\rightarrow N_A(\text{liquid}, x_A = 1) \\ N_A(\text{liquid}, x_A = 1) &\rightarrow N_A(\text{crystal}, x_A = 1). \end{aligned} \quad (6)$$

The first reaction is a density fluctuation from the mixture to a pure liquid domain of A particles, the second is crystallization. The crystallization is (qualitatively) described by classical nucleation theory (CNT). In its simplest formulation the number of particles, N^* , in the critical nucleus is given [6] by

$$N^* = \frac{32\pi\gamma_\infty^3}{3\rho_s^2 \Delta\mu_A^3}, \quad (7)$$

where γ_∞ is the solid-liquid surface tension, ρ_s is the crystal number density and $\Delta\mu_A$ is the change in Gibbs free energy per A particle by going from the crystal to pure A liquid. When the creation of a pure A crystal takes place in a mixture, the lowering of Gibbs free energy by the crystallization process is reduced by $\delta\mu = -\Delta G_{\text{mix},A} = -\Delta H_{\text{mix},A} + T_{\text{fus},A}\Delta S_{\text{mix},A} \approx -\Delta_{A,\text{mix}}u_{\text{pot}} - k_B T_{\text{fus},A} \ln(x_A)$. Since the size of the critical nucleus N^* varies as $N^* \propto (\Delta\mu_A)^{-3}$, when $\Delta\mu_A$ is replaced by $\Delta\mu_A - \delta\mu_A$ to lowest order the change in critical nucleus size δN^* is given by $\delta N^*/N^* = 3\delta\mu_A/\Delta\mu_A$, thus

$$\frac{\delta N^*}{N^*} = -3 \frac{\Delta_{A,\text{mix}}u_{\text{pot}}(x_A) + k_B T_{\text{fus},A} \ln(x_A)}{\Delta\mu_A}. \quad (8)$$

Both the negative mixing energy and the mixing entropy terms tend to increase the size of the critical nucleus. Note, however, that if the crystallization is instead to, e.g., an AB-crystal from an A-rich mixture with positive AB binding energy, the size of the critical nucleus is reduced. This prediction agrees with our simulations of crystallization in supercooled mixtures of varying composition.

The above stability considerations indicate that if a binary mixture crystallizes into, e.g., an AB-type crystal, a negative mixing energy will enhance the tendency of crystallization by decreasing the size of the critical nucleus. Confirming this, we find that increasing the fraction of B particles to $x_B=0.5$ for KA-type BLJ mixtures results in systems that more quickly crystallize into an AB (CsCl structure) crystal. This is consistent with the results of Fernandez and Harrowell [7], who found that the $T = 0$ equilibrium phase of the KABLJ mixture consists of coexisting pure A (FCC) and AB (CsCl structure) crystals.

The mixing energy term plays also an important role for the KA mixture and here we observe (see later) that the nucleation time depends on details in the truncation of the pair potentials in agreement with Eq. 8.

III. THE WAHNSTRÖM AND THE KOB-ANDERSEN BINARY LENNARD-JONES MIXTURES

The simplest case of a real mixture is that given by the semi-empirical Lorentz-Berthelot (LB) rules [8] relating the energy parameters σ and ϵ in the pair potentials between the different species of the AB mixture:

$$\sigma_{AB} = (\sigma_{AA} + \sigma_{BB})/2 \quad (9)$$

$$\epsilon_{AB} = \sqrt{\epsilon_{AA}\epsilon_{BB}} \quad (10)$$

These rules apply for atoms with weak dispersion attractions [9], and they work well for simple mixtures of for instance noble-gas atoms [8], i.e., for interactions between spherically symmetric atoms with unperturbed valence-electron orbitals.

There are two standard models for highly viscous supercooled liquids, the model introduced by Wahnström (WA) [1] and the model by Kob and Andersen (KA) [2]. Both models imply Lennard-Jones potentials. The WA model obeys the LB-rules by having

$$\sigma_{AB} = (\sigma_{AA} + \sigma_{BB})/2 \quad (11)$$

with $\sigma_{BB} = 1/1.2\sigma_{AA}$ and $\epsilon_{AB} = \epsilon_{AA} = \epsilon_{BB} = 1$. The KA model strongly disobeys the LB-rules: The LJ-potential parameters for the KA mixture are $\sigma_{AB} = 0.8\sigma_{AA}$, $\sigma_{BB} = 0.88\sigma_{AA}$, $\epsilon_{AB} = 1.5\epsilon_{AA}$, and $\epsilon_{BB} = 0.5\epsilon_{AA}$. This results in a tendency for the small solute B particles to “glue” to the A particles. This mixture has a significant non-ideal mixing energy and it is considerably more stable against crystallization than the WA mixture.

We have calculated [10] the melting point temperature in the interval $x_B \in [0, 0.2]$ for these two models, the result is shown in Figure 1. The melting point depression by mixing is traditionally given at constant pressure. Most MD simulations are, however performed for isochores where $T_{\text{fus},A}(x_B)$ depends on the partial volumes of the species in the mixture. In the case of a KA mixture the pressure decreases with an increasing fraction of small B particles at constant volume and $T_{\text{fus},A}$ is further depressed.

As can be seen from the figure the negative mixing energy lowers the melting point temperature significantly. The Wa model is indeed more prone to crystallization than the KA model and recently Pedersen and co-workers reported crystallization of the Wa model after lengthy computer runs [5]. The crystal is the MgZn₂ phase consisting of particles in the ratio 1:2, different from the 1:1 ratio defining the Wahnström BLJ. Thus concentration fluctuations precede (or at least correlate with) crystal formation. These findings inspired us to investigate whether the more widely studied KA model also crystallizes in lengthy computer runs.

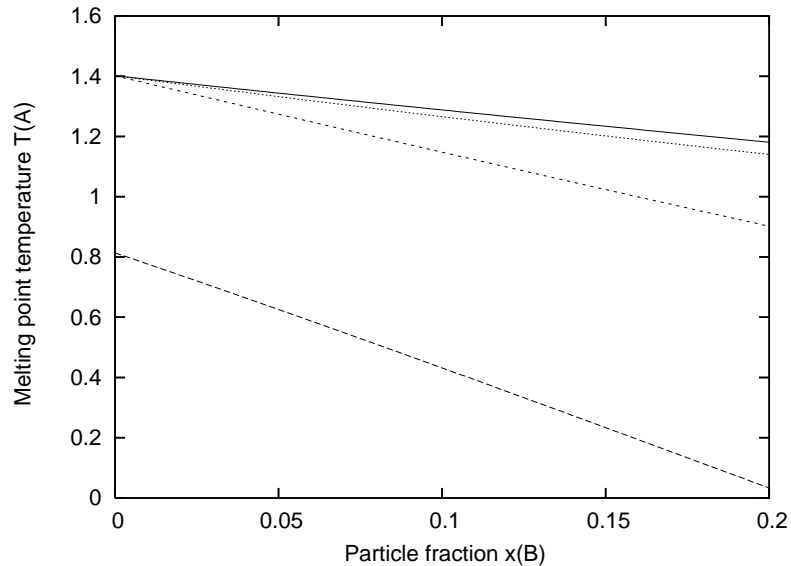


FIG. 1: Melting point temperature $T_{\text{fus,A}}$ of the solvent of A-particles at the external pressure $p=10$ as a function of the particle fraction x_B of solute particles, and in the concentration interval $x_B \in [0, 0.2]$ where the system crystallizes into a crystal of pure (fcc) A-particles. With full line is $T_{\text{fus,A}}(x_B)$ for an ideal mixture, with dots is the Wahnström-model [1], with small dashes is for the Kob-Andersen mixture [2], and with long dashes is the present modified mixture (see Sec. IV).

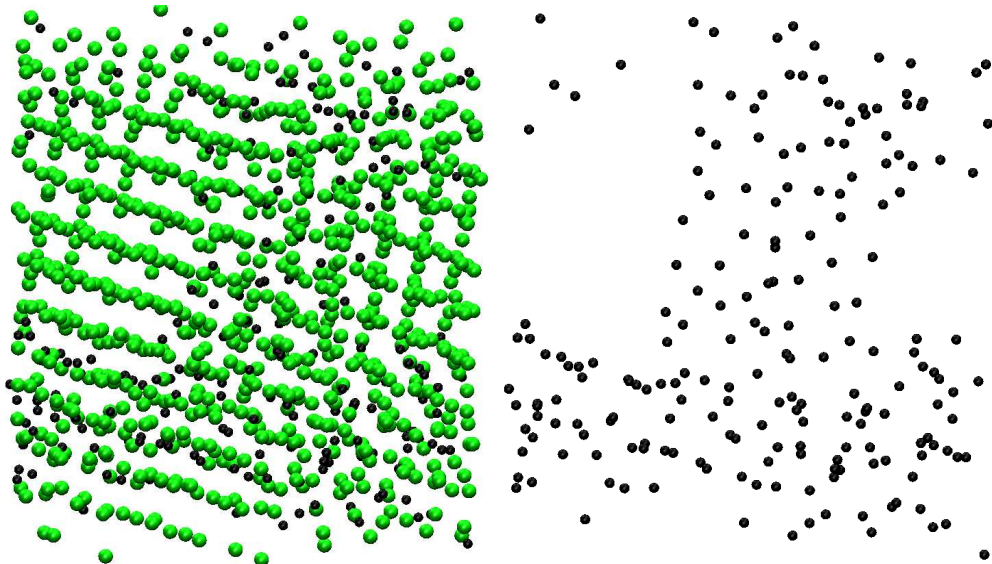


FIG. 2: (a) Particle positions projected onto a plane for the standard Kob-Andersen binary Lennard-Jones liquid (the large (A) particles are green, the small (B) particles are black). The system is shown after $1.5 \mu\text{s}$ of simulation (Argon units) at $T=0.40$ and density 1.2 (dimensionless units). After this simulation time the A particles phase separated and formed a large crystal, as is clear in the second figure showing the same configuration with all A particles removed.

We performed molecular dynamics simulations of 1000 (and 10000) particles of the standard Kob-Andersen binary Lennard-Jones liquid in the NVE and NVT ensembles. The system was simulated at the density 1.2 in dimensionless units at varying temperatures. The standard time-reversible leap-frog (NVT) algorithm [11] was used with a time step of 0.005 (in Argon units: $\approx 10^{-14}$ s). The software used has been described elsewhere [12]; it utilizes a double sorting of neighbor particles that makes it possible to simulate $1 \mu\text{s}$ within 2-3 days of computing on a standard computer.

For temperatures above 0.45 no crystallization was detected. In the temperature interval $[0.39, 0.45]$ a suspicious drop in pressure taking place typically after $\approx 10^8$ time steps indicates that something is happening. It turns out that

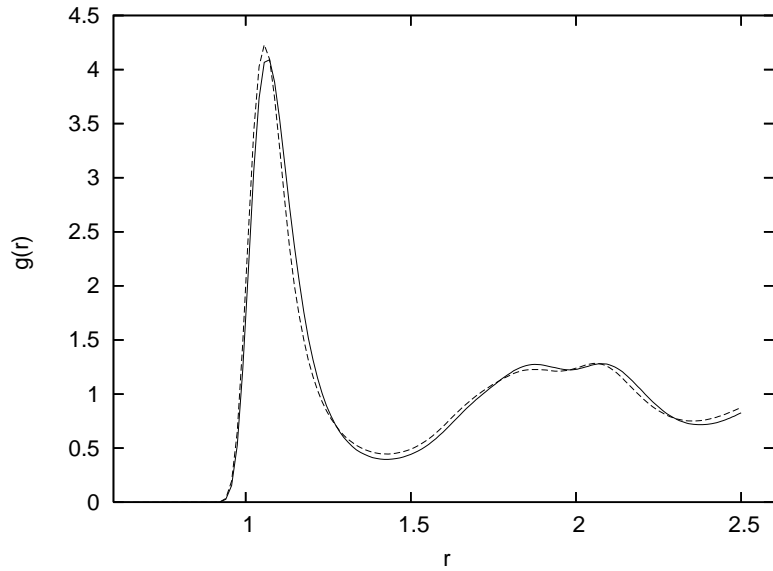


FIG. 3: Radial distribution functions $g_{A,A}(r)$ for the A-particles at the density $\rho=1.2$ and the temperature $T=0.50$ for a mixtures with particle fraction $x_B=0.2$ of B-particles. Full line is for a KA-mixture and the dashed curve is for the modified mixture.

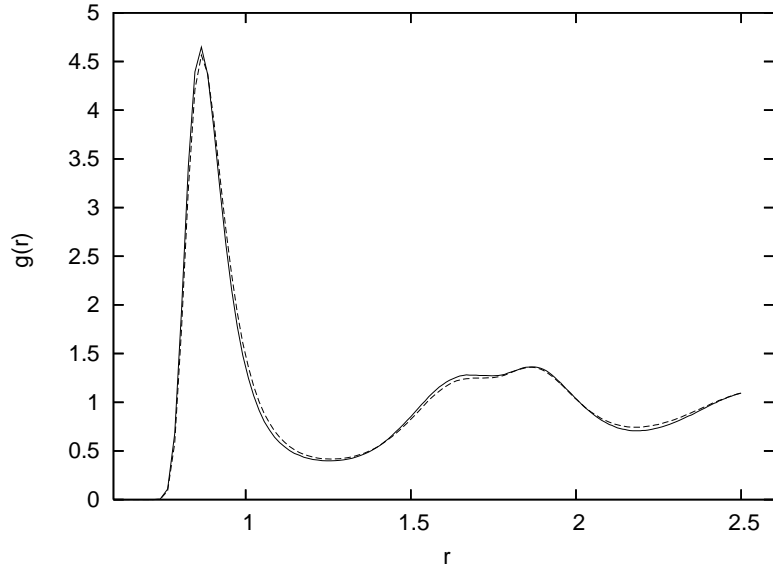


FIG. 4: The corresponding radial distribution functions $g_{A,B}(r)$ for A-B distribution.

the system phase separates such that the A particles form fairly large regions with no B particles present. Linked to this phase separation is a crystallization of the A particles. Ten simulations were performed in the $[0.39, 0.45]$ temperature interval; after $4. \times 10^8$ time steps ($\approx 4\mu s$) eight of these ten simulations phase separated with crystallization of the A particles. The general treatment of stability by supercooling a mixture indicates,

Figure 2 shows a representative example of our results, giving the positions of the particles after crystallization at $T=0.40$ (NVT-MD). There is a large region of pure A particles showing clear crystalline order.

that if a binary mixture can crystallize into e.g. a AB-type crystal, then the mixing energy can enhance the tendency of crystallization, in CNT by decreasing the size of the critical nucleus. We find that increasing the fraction of B-particles to $x_B=0.5$ results in that the KA- mixture quickly crystallizes into an AB (CsCl structure) crystal in accordance with the CNT prediction. The result is as mentioned also consistent with the results of Fernandez and Harrowell [7], who found that the $T = 0$ equilibrium phase of the KA consists of a coexisting A (fcc) and AB (CsCl structure) crystals.

The stability of the supercooled mixture depends on details in the cut-off of the potentials. Originally Kob and

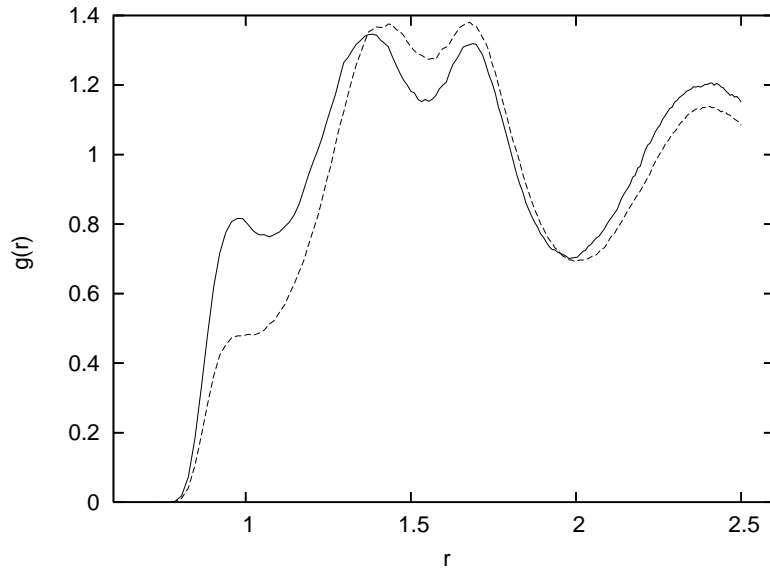


FIG. 5: The corresponding radial distribution functions $g_{B,B}(r)$ for B-B distribution.

Andersen used a cut-off at $2.5\sigma_{\alpha,\beta}$ ($\alpha, \beta = A, B$). If one instead of these values uses the same cut-off for all three pair potentials, i.e. $2.5\sigma_{A,A}$, this corresponds to a shift from $2.5\sigma_{A,B}$ to $3.125\sigma_{A,B}$. By this extension of the range of the AB attraction the mixing energy becomes more negative than in the original KA mixture by an amount of $0.04\epsilon_{A,A}$. This may seem insignificant, but according to Eq. (8) the corresponding change in the critical nucleus size is of order 10%. Consistent with this we find that the KABLJ mixture with this cutoff must be simulated typically three times longer before it crystallizes than when using the original KA parameters.

IV. A MODIFIED BINARY MODEL SYSTEM NOT PRONE TO CRYSTALLIZATION

With the general theory for melting point depression and nucleation in mind it is possible to modify the existing models in such a way that they are not prone to crystallization. We want to maintain the success of the existing models, which are set up to simulate real supercooled mixtures, in the case of KA-model a binary mixture of $\text{Ni}_{80}\text{P}_{20}$ alloy. For this reason the sizes of the molecules in the KA-mixture, given by the σ_{ii} values, are maintained. We also want to have the same structure of the KA-mixture, given by their correlation functions. A modified KA-mixture with only repulsive forces between A-A and B-B particles, but where the attraction between A- and B-particles is maintained

$$u_{ij}(r_{ij}) = \begin{cases} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] - u_{LJ}(r_{ij}(\text{cut})), & r_{ij} < r_{ij}(\text{cut}) \\ 0, & r_{ij} \geq r_{ij}(\text{cut}), \end{cases} \quad (12)$$

with

$$r_{i,i}(\text{cut}) = 2^{1/6}\sigma_{i,i} \quad (13)$$

$$r_{A,B}(\text{cut}) = 2.5\sigma_{A,B} \quad (14)$$

meets these requirements. *A priori* it is to be expected [13] that the structure of the mixture only deviates marginally from the originally KA-model because the repulsive parts of the potential interactions are not changed from the original KA-model. The modified binary model is indeed much more stable and we have so far not been able to crystallize the mixture (for a particle fraction $x_B = 0.2$). There are two reasons for this resistance against crystallization by supercooling. Firstly the melting point temperature, $T_{\text{fus},A}^*$, of the pure solvent particles is lowered significantly (see Figure 1) and secondly the relative importance of the mixing energy, $\Delta_{A,\text{mix}}u_{\text{pot}}(x_B)$, is bigger due to a stronger violation of the LB-rules for the energy and thereby a lower melting point temperature and an increase of the size

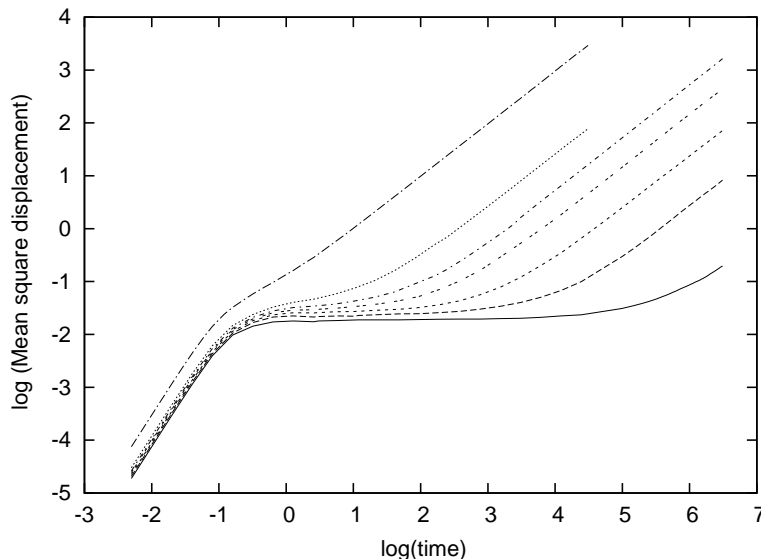


FIG. 6: $\log - \log$ plot of the mean square displacement for A-particles as a function of time (in unit $\sigma\sqrt{m/\epsilon} \approx 2. \times 10^{-12} s$) and for different temperatures (from the left): $T=1.00, 0.40, 0.35, 0.325, 0.30, 0.275$ and 0.25 . respectively.

of the critical nucleus. Another advantage of the modified system is that it is much faster to simulate by using a two-step sorting of nearest neighbor [12]. In addition to that one can use a bigger value of the time increment in the MD simulation due to the lower temperature, so not only does the mixture not crystallize; but it can also be cooled further down under equilibrium condition (see Figure 6-8) and followed a much longer times ($0.1ms$).

The structure of the modified mixture is, as expected, almost the same as in the KA-mixture. Figure 3-5 show the radial distribution functions, $g_{\alpha,\beta}(r)$ for the modified mixture and for the KA-mixture. The similarity is well known. (The so-called WCA- system [13] with only repulsive LJ forces has been used in perturbation theories for dense liquid.) As can be seen from the figures only the distribution, $g_{B,B}(r)$ of the B-particles is affected. This change in $g_{B,B}(r)$ is due to the relative increased "binding-energy" between the solvent A-particles and the solute of B-particles which, however, is not so visible in $g_{A,B}(r)$ due to the many A-B configurations (notice the different y-scales of the two figures).

The KA- and the modified mixture were cooled down from $T=1.5$. The KA- mixture crystallizes as mentioned in the temperature interval $T \in [0.39, 0.45]$; but it is possible to quench the KA-system down to $T=0.375$ and still determine the self diffusion constant, D . The modified mixture can be cooled down to $T=0.25$, where the system was followed $10^{10} \approx$ one $0.1ms$ time step and with a diffusion constant for the A-particles, $D(A) \approx 1. \times 10^{-08}$. The B-particles behave in a similar way; but as the temperature is decreased the ratio $D(B)/D(A)$ changes from 1.7 for $T=1.5$ to 9.7 for $T=0.25$. The values of the self-diffusion constants $D(T)$ were obtained from the slopes of the mean square displacements as a function of the time. A log log-log plot of $D(T)$ for different temperatures are shown in Figure 6. At the low temperatures the ballistic- and diffusive time-regimes are very well separated.

The diffusion constants for A- and B-particles are shown in Figure 7 together with low temperature data for the KA-mixture (A-particles) [14]. It is possible to scale the diffusion constants for the two mixtures as is demonstrated in Figure 8, where $\log(D)$ for the KA-mixture (+) connected with dots, is plotted as a function of $1/(T*0.81)$. A similar behavior for "fragility invariance" for systems with the same repulsive potentials has been observed before [15].

V. DISCUSSION

The highly viscous fluid state below the equilibrium melting point temperature is found in many systems ranging from simple organic one-component systems and alloys to complex biochemical substances and ionic liquids. Along with the increasing interest in this state of matter it is important to have models not prone to crystallisation. The general thermodynamics theory for (equilibrium) melting and classical nucleation theory gives an indication of how

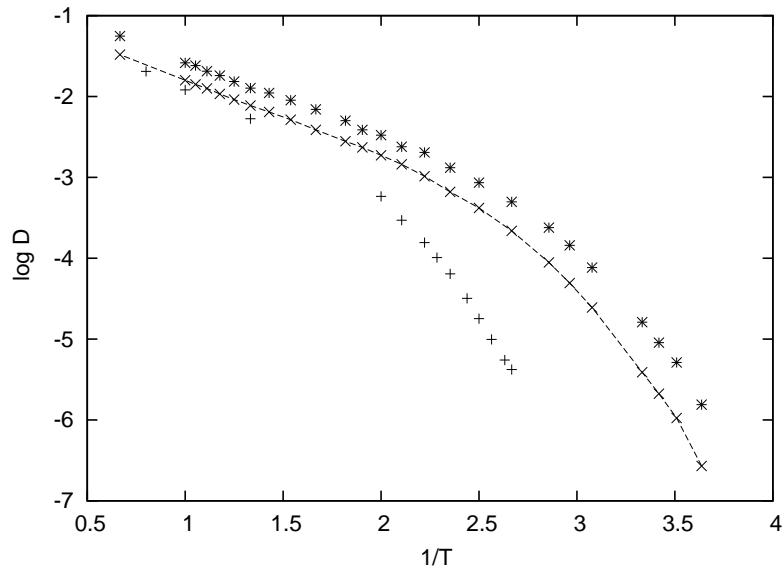


FIG. 7: An Arrhenius plot, $\log D(1/T)$, of the self diffusion constant D . With + is $D(A)$ for the KA mixture, and the points given by \times and connected with lines is $D(A)$ for the modified binary mixture (see III B). The diffusion constants, $D(B)$ for the smaller B-particles in the modified binary mixture are shown with \star .

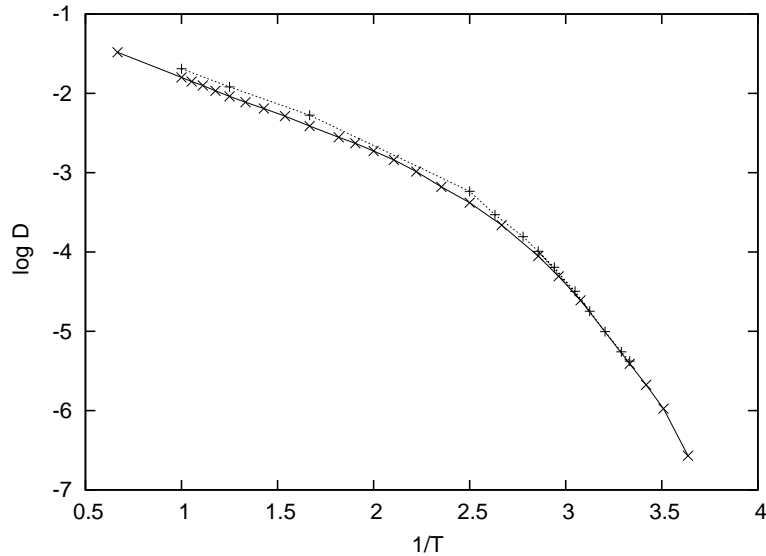


FIG. 8: With full line is the $\log D(1/T)$ for the modified mixture (the data points from Fig.8 are just connected by straight lines) and with dashes are the corresponding scaled KA-data $\log(D)(\frac{1}{0.81T})$.

to create models which suppress crystallisation by cooling. We have given one simple example by modifying the Kob-Andersen model which is the most used MD model for binary highly viscous fluids but it is straight forward to extend the model to include other interactions and a more refined energy functions without loose its stability against crystallization. A general recipe of energy functions for stable highly viscous liquids are, however difficult to set up since many mixtures exhibits "reacting systems" with crystals with mixed compositions where an increased binding-or mixing energy can enhance crystallization of e.g. A,B crystals. Both the Kob-Andersen and the Wahnström models are examples of this phenomenon.

The modified model enhances the relative attraction between unlike species by removing the attraction between the A,A- and B,B-interactions. Supercooled liquid (WCA-) mixtures with solely repulsive LJ-potentials have been reported before [16], [17]; but we observe that both systems [16], [17] phase separate and crystallized by cooling.

By maintaining the attraction between unlike species the highly viscous state is stabilized. The modified mixture disobeys the LB-energy rule much more than the KA-mixture. The LB-energy rule is a geometric mean of interaction energy between two particles with energy scaling parameters, ϵ_{AA} and ϵ_{BB} . The two models have the same energy scaling parameters, $\epsilon_{\alpha\beta}$; but a much stronger violation of the energy rule in the interaction interval $r_{\alpha\beta} \in [2^{1/6}\sigma_{i,i}, \infty]$ where the WCA-potentials are zero. The result of this "cut and shift" is that the B-particles are almost "covalent" bounded to the A-particles and the violation of the LB-rule for the mixing energy gives recipe of creating fragile and stable supercooled liquid mixtures.

Acknowledgments

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